

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. :

U.S. National Serial No. :

Filed :

PCT International Application No. : PCT/EP2004/005882

VERIFICATION OF A TRANSLATION

I, Susan ANTHONY BA, ACIS,

Director of RWS Group Ltd, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare:

That the translator responsible for the attached translation is knowledgeable in the German language in which the below identified international application was filed, and that, to the best of RWS Group Ltd knowledge and belief, the English translation of the international application No. PCT/EP2004/005882 is a true and complete translation of the above identified international application as filed.

I hereby declare that all the statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application issued thereon.

Date: October 27, 2005

Signature :



For and on behalf of RWS Group Ltd

Post Office Address :

Europa House, Marsham Way,  
Gerrards Cross, Buckinghamshire,  
England.

## Description

Method and device for producing melamine in a single-phase tubular reactor

5

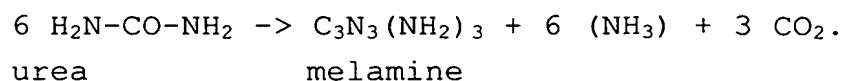
The invention relates to a process according to the preamble of Claim 1 and to an apparatus according to the preamble of Claim 14.

10 The characteristic substance properties of every pure substance are a critical temperature, a critical pressure and a critical volume. When a substance is in the supercritical state, there no longer exists any division between a liquid phase and a gas phase. The supercritical fluid behaves in a  
15 unique manner. For example, a supercritical substance may have a viscosity of a gas at the density of a liquid. The variation of the pressure and of the temperature conditions allows the flow properties of a substance usually to be precisely influenced within wide limits.

20

In a mixture of supercritical substances (for example ammonia and carbon dioxide) with subcritical substances (depending on temperature, for example, melamine), complete miscibility may lead to mixture properties which correspond to those of  
25 supercritical substances. This means that the mixture is in monophasic form.

It is known (see, for example, Ullmann's Encyclopedia of Industrial Chemistry, 5<sup>th</sup> edition, vol. A16, p. 171 ff) that  
30 melamine can be prepared by thermal conversion to melamine according to



35

In this reaction, molten urea ( $T_{\text{melt}} = 132^\circ\text{C}$ ) is used. The reaction product obtained is melamine,

ammonia and carbon dioxide. Ammonia and carbon dioxide are referred to together as offgas.

In principle, there are two preparation processes for  
5 melamine, i.e. noncatalytic, high-pressure processes and catalytic low-pressure processes.

In low-pressure processes, a gas phase reaction is carried out at pressures of typically 10 bar and temperatures between  
10 390 and 410°C. In the high-pressure processes, a liquid phase reaction is carried out at temperatures between 370 to 425°C and pressures between 70 and 150 bar.

In both process variants, there is the disadvantage that  
15 large amounts of offgas are obtained. Since these substances are in the gas phase under the reaction conditions, the reactor in particular has to be designed with appropriately large dimensions. Since the reaction mixture is strongly corrosive, the relatively large reaction vessels have to be  
20 manufactured from special material, for example titanium.

Use of a compact tubular reactor under these conditions is not an option, since the offgas very rapidly shifts the unconverted urea out of the reactor. There would be a  
25 biphasic reaction mixture. Moreover, the heat transfer under these conditions is poor, so that very large heat transfer surfaces are required in order to introduce the high heat of reaction, which further greatly complicates the reactors.

30 It is an object of the present invention to provide a process and an apparatus by which a more efficient reaction to give melamine is possible.

This object is achieved in accordance with the invention by a  
35 process having the features of Claim 1.

According to the invention, the reaction of urea to melamine proceeds at least partly under reaction conditions under which at least one reactant, intermediate and/or end product is in a supercritical state. The mixture of at least one  
5 reactant, intermediate and/or end product also forms a substantially homogeneous phase, and all reactants, intermediates and/or end products are in particular fully dissolved.

10 The use of a "supercritical mixture" allows monophasicity to be established, by which the reactor volume can be greatly reduced.

This allows material and building space to be saved. This  
15 also leads to improvements from a safety viewpoint, since the amount of substance under high pressure is smaller. The high pressure additionally also improves the melamine quality, since the proportion of by-products is reduced. The supercritical substance properties lead, at a corresponding  
20 flow rate which is achievable with acceptable pressure drop owing to these substance properties, to a very high heat transfer number, which permits the input of the reaction energy required via the relatively small tube wall surface area.

25 It is advantageous when the reaction proceeds at least partly at a pressure above 550 bar, in particular between 600 and 800 bar. In an advantageous manner, the reaction proceeds at least partly at a temperature of at least 350°C, in  
30 particular 400°C.

In an advantageous embodiment of the process according to the invention, the reaction proceeds in a continuous tubular reactor. It is particularly advantageous when the tubular  
35 reactor is at least partly heated to obtain the reaction temperature.

It is also advantageous when liquid urea is used as the reactant.

5 The attainment of the reaction pressure is advantageously brought about upstream of the reactor by a high-pressure pump which conveys the liquid urea.

10 In a further advantageous embodiment of the process according to the invention, the reaction product of the reactor is decompressed, to solidify the melamine, into a decompression vessel having a pressure of less than 200 bar, in particular atmospheric pressure.

15 The decompression from a very high pressure results in distinct cooling. Advantageously, the decompression vessel is heatable.

20 It may be advantageous when an offgas formed in the decompression vessel has at least the pressure of a urea synthesis, so that it can be fed to a urea synthesis plant.

25 It is also advantageous when the inventive apparatus has a decompression apparatus, especially a valve for controlled decompression into the decompression vessel.

In addition, it is advantageous when a regulation apparatus for pressure regulation is provided in the reactor, particularly when the regulation apparatus for the reactor pressure is coupled to the decompression apparatus.

30 The object is also achieved by an apparatus having the features of Claim 13, in which a reactor is designed as a tubular reactor for supercritical reaction conditions. Such a reactor may have a very compact construction.

In an advantageous manner, the tubular reactor comprises a titanium alloy in order to be protected against corrosive media.

- 5 It is also advantageous when the inventive apparatus has a decompression apparatus for decompression of reaction products into a decompression vessel.

10 The invention is illustrated hereinbelow with reference to the figures of the drawings using a working example. The figures show:

Fig. 1 a process flow diagram for a supercritical melamine process;

15

Fig. 2a-2d measurements for the change in the volume as a function of the pressure.

20

Fig. 1 shows one embodiment of the process according to the invention. This is the production of melamine (2,4,6-tri-amino-1,3,5-triazine,  $C_3N_6H_6$ ) from urea (carbamide,  $CO(NH_3)_2$ ).

To this end, urea is initially charged in a reservoir vessel 1 and fed as required to a reactor 4.

25

The urea in the reservoir vessel 1 is initially charged at a temperature of somewhat more than  $132^{\circ}C$ . Subsequently, the urea melt is brought by a high-pressure pump 3 (for example membrane piston pump or gear pump) to a pressure level which  
30 is sufficiently high that the subsequent reaction in the reactor 4 can proceed substantially monophasically.

The phase behaviour may be determined by measuring the volume change as a function of the temperature at constant pressure.

35

At low, constant

pressures (e.g. 130 bar), i.e. when a biphasic mixture is present, a sharp rise in volume with rising temperature can be seen; a gaseous phase forms. When the same measurement is carried out at a higher pressure (e.g. 800 bar), it can be  
5 seen that the volume increase rises with increasing temperature without a sharp increase; no new phase is formed. In addition, the amount of heat required for the heating can be determined in a calorimeter.

10 In order to achieve monophasicity, the pressure in the reactor 4 will be above 550 bar, preferably in the range from 600 to 800 bar.

To achieve an acceptable conversion, the reactor 4 is heated  
15 to at least 350°C, preferably around 400°C. To this end, the reactor 4 is brought to the process temperature over its length using a heater 41. Under these conditions, the reaction mixture is present in a single phase. In this case, the flow is configured as plug flow, so that intensive heat  
20 transfer can be established.

The offgases which are otherwise present as a second phase are a portion of the reaction mixture having supercritical material properties. The reactor 4 is configured as a  
25 continuous tubular reactor.

Downstream of the reactor 4, the reaction products (melamine, ammonia, carbon dioxide,  $\text{NH}_2\text{COONH}_4$ ,  $\text{NH}_2\text{CONH}_2$ , residues of urea (for example 15%)) are passed via a decompression apparatus 5  
30 into a decompression vessel 6.

The decompression apparatus 5 is configured as a valve. The decompression of the reaction products results in a pressure being formed in the decompression vessel 6. A low pressure  
35 may be selected in order to keep the plant costs low, but a pressure of about 200 bar may also be selected,

in order to conduct the offgas back into a urea plant. Quenching in, for example, ammonia or water is also conceivable.

5 The temperature in the decompression vessel 6 may be selected between room temperature and the hydrolysis or decomposition temperature of melamine. The melamine solidifies very rapidly or can be dissolved in the quench medium. The decompression vessel 6 is equipped with a heating apparatus which allows  
10 heating or cooling as desired. The heating may influence, for example, the physical state of the melamine, within wide limits.

The valve 5 also serves as the actuator for a regulation  
15 apparatus 42 which is configured here as a PI regulator. In principle, other regulation mechanisms, for example multiparameter regulation systems, may of course also be used. Safety valves or safety regulation systems which are needed under some circumstances are also not shown here.

20 After the decompression, the gaseous offgases are removed out of the top of the decompression vessel 6. When the decompression vessel 6 is appropriately heated, the carbamate ( $\text{NH}_2\text{COONH}_4$ ) may be thermally decomposed into carbon dioxide  
25 and ammonia (offgas). At a suitable pressure level in the decompression vessel 6, the offgas may be recycled into the high-pressure section of a urea synthesis.

The constituents which are solid or have been taken up in the  
30 quench medium (melamine,  $\text{NH}_2\text{COONH}_4$ ,  $\text{NH}_2\text{CONH}_2$ ) are discharged from the decompression vessel 6 and are then conducted to a further processing step 7, for example a finishing step or to a recrystallization step not illustrated here in more detail to a scrubbing step.

35 Fig. 2a to 2d illustrate measurements which were obtained in the preparation of melamine in the presence of ammonia and carbon dioxide. Each shows the



change in the volume as a function of the temperature. The pressure was in each case kept constant.

At the lowest pressure of 130 bar (Fig. 2a), it can be seen  
5 that there is a great increase in volume above approx. 265°C,  
i.e. a second, gaseous phase forms. At the next pressure  
stage of 350 bar (Fig. 2b), the pressure increase above 300°C  
is no longer quite so severe; the gradient is lower. This  
trend continues at 600 bar (Fig. 2c). An evaporation might  
10 take place in the range from 300 to 350°C.

Fig. 2d finally shows the volume increase at a pressure of  
800 bar. It is virtually impossible to see an abrupt increase  
in volume. This shows that the mixture of reactants,  
15 intermediates and end products forms a substantially  
homogeneous mixture whose volume grows relatively constantly  
with the temperature.

The performance of the invention is not restricted to the  
20 above preferred working examples. Rather, a number of  
variants is conceivable which make use of the process of the  
invention and of the apparatus of the invention, even in  
embodiments which are fundamentally of a different nature.

Reference numeral list .

- 1     Reservoir vessel
- 3     High-pressure pump
- 4     Reactor
- 5     Decompression apparatus
- 6     Decompression vessel with heating unit
- 7     Further processing step